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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C10L 1/02, 1/10, 1/18

A1

(11) International Publication Number: WO 95/02654

(43) International Publication Date: 26 January 1995 (26.01.95)

(21) International Application Number: PCT/AU94/00401

(22) International Filing Date: 15 July 1994 (15.07.94)

(30) Priority Data:
PM0004 16 July 1993 (16.07.93) AU

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(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD).

Published
With international search report.

(54) Title: FUEL BLENDS

(57) Abstract

A fuel blend composition including a hydrocarbon liquid as defined, up to 20 % of the total composition of ethanol and/or n-propanol and up to 15 % by volume of the total composition of a fatty acid and/or organic ester.

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FUEL BLENDS

Field of the Invention

This invention relates to fuel blend compositions including a hydrocarbon liquid, low-alkyl alcohol and fatty acid and/or organic ester. Additionally, the invention relates to a fuel additive composition including a low-alkyl alcohol and fatty acid and/or organic ester.

Background to the Invention

Diesel oil, due to its cost and availability, continues to be the backbone for industry around the world being the principal fuel for use in trucks, ships, trains, some cars and other automotive equipment and different stationary types of engines.

It is well recognised that the combustion of diesel fuel in engines can be hazardous to the environment. In particular, the partial combustion of diesel fuel to carbon, carbon monoxide, and nitrogen oxides creates noxious black exhaust gases which are pollutants. This problem is particularly observable in trucks and other automotive vehicles where noxious black exhaust gases can be seen being released into the environment.

Attempts have been made over the years to address the environmental concerns associated with exhaust fumes from engines by using alcohols such as methanol (methyl alcohol) or ethanol (ethyl alcohol) as fuels. Such attempts, for instance, have generally established that 15% of ethanol and 85% diesel oil provides an acceptable burning capacity without the necessity of modifying existing diesel engines.

The problem with using ethanol or methanol as a fuel in conjunction with diesel oil is that ethanol or methanol are immiscible with diesel oil, that is, they cannot be uniformly mixed or blended into one phase without rapid separation into their component parts. Since they cannot be uniformly mixed into one phase and stored for easy use, the components must be mixed just prior to use by, for example, having independent fuel tanks with the components independently pumped and mixed just before the combined fuel is injected into the fuel chamber. Such a system is currently being used in the bus fleet of the Des Moines Transit Authority, Iowa, USA.

One attempt to address the problem of immiscibility was to form an emulsion of the diesel oil and ethanol using an emulsifier. An example of this is in Australian Patent No. 544,728 which discloses a composition having 84.5% diesel oil, 15% hydrated ethanol and 0.5% emulsifier. The emulsifier is of the styrene butadiene co-polymer type in admixture with a high molecular weight polyethylene glycol dissolved in xylene. This mixture can show both batch to batch variation and instability as the diesel and ethanol separate in the fuel tank.

An attempt has also been made to address the problem of immiscibility by forming a blend comprising a petroleum fuel, methanol and a higher alcohol having 10-16 carbon atoms as a solvent for the petroleum fuel and methanol. An example of this is disclosed in US Patent No. 4,527,995.

A further attempt to address the problem of immiscibility is disclosed in UK Patent Application No. GB 2,090,611 where combustible compositions are claimed containing gas oils, methanol and a fatty acid ester for use in diesel engines. The claimed combustible compositions comprises from 20% to 90% by volume of at least one gas oil, from 5% to 50% by volume of methanol and from 5% to 60% by volume of at least one (C_1 - C_3) alkyl ester of a (C_6 - C_{22}) saturated or unsaturated fatty acid. The specification states that alcohols heavier than methanol such as butanol must be added in substantial portions and do not improve the cetane number.

The article entitled "Diesel Oil Substitution by Processed Plant Oils - Engine and Vehicle Results" published in 1982 by two authors from Volkswagen do Brasil S.A. Brazil, compares tests conducted using a straight methyl ester of soya bean oil (MESO) as a fuel with a 75-25 gasoil-MESO blend and a 68-23-9 gasoil-MESO-ethanol (anhydrous) blend. The article provides that plant-oil mono-esters used as gasoil extenders serve as co-solvents between gasoil and ethanol, thus permitting ready use of otherwise-incompatible ethanol. However, the article provides that an increase in proportion of ester in the gasoil from a 25% ester content onwards results in the ethanol being substantially compatible in the gasoil.

In subsequent investigations leading to the present invention, it has surprisingly been found that fatty acids and/or organic esters having up to 15% by volume in the fuel blend composition function as a coupling agent between the hydrocarbon liquid and ethanol and/or n-propanol to form a single phase composition which is not prone to separation.

Summary of the Invention

According to a first embodiment of the invention, there is provided a fuel blend composition including a hydrocarbon liquid (as hereinafter defined), up to 20% by volume of the total composition of ethanol and/or n-propanol and up to 15% by volume of the total composition of a fatty acid and/or organic ester.

In a preferred embodiment of the invention, the fatty acid and/or organic ester component is between 1.5% and 11% by volume.

In another preferred embodiment of the invention, the fatty acid and/or organic ester component is between 2% and 5% by volume.

The fatty acid component is derived preferably from natural oils and fats such as lard, tallow and vegetable oils, for example, canola, palm, corn, sunflower and soya bean oils or from specific blends commercially produced by fatty acid manufacturers or from fatty acids made by synthetic means or mixtures thereof. The fatty acid is preferably "oleic acid". For those skilled in the art, this is understood to mean the commercially available liquid fatty acids in which the mono-unsaturated fatty acid is significantly present.

The organic ester component is selected preferably from fatty esters such as ethyl oleate, ethyl tallowate, iso-propyl oleate, butyl oleate, methyl oleate or methyl cocoate and/or other aromatic esters such as butyl benzoate and/or other aliphatic esters such as ethyl acetate or mixtures thereof and/or dicarboxylic acid esters such as dioctyl maleate.

In another preferred embodiment of the invention, the fuel blend composition also includes methanol, butanol, iso-butanol, tert-butanol or mixtures thereof.

In a preferred embodiment of the invention, the hydrocarbon liquid (as hereinafter defined) component is at least 40% by volume of the total composition and more preferably between 75% and 88%.

The term hydrocarbon liquid, as used in the specification, means diesel oil and gas oil and mixtures thereof.

According to a preferred embodiment of the invention, there is provided a process for producing a single phase fuel blend composition including the steps of:

(a) adding the ethanol and/or n-propanol to the hydrocarbon liquid to form a mixture at the alcohol phase and an oil phase and thereafter;

(b) adding the mixture of step (a) to the fatty acid and/or organic ester; and

(c) mixing the resultant mixture until a single phase has been formed.

According to a further embodiment of the invention, there is provided a fuel additive composition including ethanol and/or n-propanol and a fatty acid and/or organic ester in respective amounts ranging from a ratio of 25:1 to 1:1. Up to 35% of the fuel additive composition is added to the hydrocarbon liquid to form a single phase composition.

In a further preferred embodiment of the invention, a process to produce a single phase fuel blend composition is provided by:

(a) adding the ethanol and/or n-propanol and the fatty acid and/or portion of organic ester to form the additive composition and thereafter;

(b) adding the mixture of (a) to the hydrocarbon liquid ; and

(c) mixing the resultant mixture until a single phase has been formed.

Examples

The carboxylate esters used in the examples are those manufactured at the premises of the Victorian Chemical Co., Richmond, Victoria, Australia and are sold under the "Esterol" brand name. The ethyl acetate was purchased from BP Chemicals Australia. The diesel oil is that purchased from pumps of major Australian oil companies such as Caltex Petroleum Pty Ltd. The ethanol (ethyl alcohol) is commercial material obtained from the CSR Distilleries, Yarraville Victoria, Australia and is known as Ethanol 100SG/F3 which contains 3% methanol.

The following is a non-limiting example of a process to produce Composition 1 below according to the invention.

Diesel oil (85ml) is placed in a 100ml bottle at ambient temperature and pressure. Ethanol (10.0 ml) is added to the bottle creating an oil phase and an alcohol phase. Methyl oleate (5.0ml) is then added, a stopper applied to the top of the bottle and the resultant mixture is shaken for a period of approximately 30 seconds or such less or further period of time to allow proper mixing of the liquids to take place and a single phase to form. The mixture was allowed to stand to allow the contents to settle. A single phase is observed.

Substantially the same method is used to produce the other compositions detailed below.

Product blends were made (as percentage v/v) as follows.

Composition 1

Diesel Oil	85.0
Ethanol	10.0
Methyl Oleate	5.0
	100.0

Composition 2

Diesel Oil	80.0
n-Propanol	13.5
Methanol	1.5
Ethyl Oleate	5.0
	100.0

Composition 3

Diesel Oil	80.0
Ethanol	15.0
Ethyl Acetate	5.0
	100.0

Composition 4

Diesel Oil	80.0
Ethanol	15.0
Ethyl Tallowate	5.0
	100.0

Composition 5

Diesel Oil	82.0
Ethanol	15.0
Butyl Benzoate	3.0
	100.0

Composition 6

Diesel Oil	82.0
Ethanol	15.0
Oleic Acid	3.0
	100.0

Composition 7

Diesel Oil	83.0
Ethanol	13.5
Iso-Propanol	1.5
Ethyl Oleate	2.0
	100.0

Composition 8

Diesel Oil	81.0
Ethanol	15.0
Ethyl Tallowate	1.5
Ethyl Acetate	2.5
	100.0

Composition 9

Diesel Oil	80
Ethanol	14
Methanol	1
Ethyl Oleate	4
Butyl Benzoate	1
	100

Composition 10

Gas Oil	74.5
Ethanol	20.0
Oleic Acid	3.0
Iso-Propyl Oleate	2.5
	100.0

Composition 11

Diesel Oil	87.75
Ethanol	9.0
Ethyl Oleate	3.25
	100.0

Composition 12

Diesel Oil	94
Ethanol	5
Ethyl Oleate	1
	100

Compositi n 13

Diesel Oil	94.5
Ethanol	5.0
Ethyl Oleate	0.5
	100.0

Composition 14

Diesel Oil	94.8
Ethanol	5.0
Ethyl Oleate	0.2
	100.0

Composition 15

Diesel Oil	80
Ethanol	10
Ethyl Oleate	5
n-Butanol	5
	100

Composition 16

Diesel Oil	79
Ethanol	10
Ethyl Oleate	6
Iso-Propanol	5
	100

Composition 17

Diesel Oil	74
Ethanol	15
Ethyl Oleate	11
	100

Composition 18

Diesel Oil	94.8
Ethanol	5.0
Oleic Acid	0.2
	100.0

Composition 19

Diesel Oil	94
Ethanol	5
Oleic Acid	1
	100

Composition 20

Diesel Oil	88.5
Ethanol	10.0
Oleic Acid	1.5
	100.0

Composition 21

Diesel Oil	82
Ethanol	15
Oleic Acid	3
	100

Composition 22

Diesel Oil	81.5
Ethanol	15.0
Ethyl Oleate	3.5
	100.0

C mposition 23

Diesel Oil	76
Ethanol	20
Oleic Acid	4
	100

Composition 24

Diesel Oil	74.5
Ethanol	20.0
Oleic Acid	3.0
Isopropyl Oleate	2.5
	100.0

Composition 25

Diesel Oil	70
Ethanol	15
Methyl Cocoate	15
	100

Composition 26

Diesel Oil	77
Ethanol	15
Methyl Cocoate	8
	100

Composition 27

Diesel Oil	75
Ethanol	15
Methyl Cocoate	10
	100

Composition 28

Diesel Oil	78.5
Ethanol	0.5
Ethyl Oleate	6.5
n-Propanol	14.5
	100.0

Composition 29

Diesel Oil	85
Ethanol	10
Methyl Oleate	5
	100

Composition 30

Diesel Oil	77.5
Ethanol	15.0
Ethyl Oleate	5.0
Ethyl Acetate	2.5
	100.0

Composition 31

Diesel Oil	77
Ethanol	15
Dioctyl maleate	8
	100

Composition 32

Diesel Oil	65
Ethanol	20
Ethyl Oleate	15
	100

C mposition 33	
Diesel Oil	67
Ethanol	18
Ethyl Oleate	15
	100

All of the above Compositions had a single phase demonstrating the effectiveness of the use of levels of fatty acids and/or organic esters or mixtures thereof to blend hydrocarbon liquids such as diesel oil and low-alkyl alcohols such as ethanol into one phase. These compositions were tested over the typical temperatures in which normal fuels are to perform and were not found to be temperature sensitive.

In each of the Compositions listed above, the blend of diesel oil and low alkyl alcohol is in one phase and the blend was found to operate satisfactorily as a fuel.

Volkswagon Engine: A 1979 Volkswagon "Golf" 4 cylinder 1.5 litre diesel engine was tested over the several months on Composition No 15. The engine was tested under normal operating conditions and no decrease in either power or fuel efficiency was noticed.

Prime Mover Engine: A modern Mercedes Benz Prime Mover Engine Type 2228V Series was tested on Composition No 4, under typical 40 tonne loads. There was no noticeable decrease in either power or fuel efficiency of the engine.

Fork Lift Engine: A 4 cylinder Yale Forklift (Model GDP 050 RUAS) (with a) 44HP (2400 rpm) Mazda XA series diesel motor engine was tested under typical warehouse operating conditions on Composition Nos 15 and 21 over several months. As well as no difference being noted in the efficiency of the forklift engine, the use of the ethanol blend is likely to be more acceptable in the enclosed warehouse atmosphere.

In respect of each of the above compositions, a fuel additive composition can be formed of the low-alkyl alcohol and the fatty acid and/or organic ester which may be added to the hydrocarbon liquids.

Fuel Additive Compositions

The Additive Composition is illustrated by the following non-limiting examples. The following is a non-limiting example of a process to produce Additive Composition 1 below according to the invention.

Ethanol (66.7 ml) is placed in a 100 ml bottle at ambient temperature and pressure. Methyl Oleate (33.3 ml) is added to the bottle to form a clear Additive Composition 1. Additive Composition 1 (15 ml) is then added to diesel oil (85 ml), a stopper applied to the top of the bottle and the resultant mixture is shaken for a period of approximately 30 seconds or

less or for the period of time to allow proper mixing of the liquids to take place and a single phase to form.

Substantially the same method is used to produce other Additive Compositions as detailed below.

Additive Compositions were made (as percentages v-v) as follows:

Additive Composition 1

Ethanol	66.7
Methyl Oleate	33.3
	100.0

Additive Composition 1 (15 ml) was added to diesel oil (85 ml).

Additive Composition 2

Ethanol	75
Ethyl Tallowate	25
	100

Additive Composition 2 (20 ml) was added to diesel oil (80 ml).

Additive Composition 3

Ethanol	79.4
Ethyl Oleate	11.8
Iso Propanol	8.8
	100.0

Additive Composition 3 (17 ml) was added to diesel oil (83 ml).

Additive Composition 4

Ethanol	78.9
Ethyl Acetate	13.2
Ethyl Tallowate	7.9
	100.0

Additive Composition 4 (19 ml) was added to diesel oil (81 ml).

Additive Composition 5

Ethanol	50
Ethyl Oleate	25
n Butanol	25
	100

Additive Composition 5 (20 ml) was added to diesel oil (80 ml).

Additive Composition 6

Ethanol	83.3
Oleic Acid	16.7
	100.0

Additive Composition 6 (24 ml) was added to diesel oil (76 ml).

Additive Composition 7

Ethanol	78.4
Oleic Acid	11.8
Iso Propyl Oleate	9.8
	100.0

Additive Composition 7 (25.5 ml) was added to diesel oil (74.5 ml).

Additive C mposition 8

Ethanol	50
Methyl Cocoate	50
	100

Additive Composition 8 (30 ml) was added to diesel oil (70 ml).

Additive Composition 9

Ethanol	66.7
Ethyl Acetate	11.1
Ethyl Oleate	22.2
	100.0

Additive Composition 9 (22.5 ml) was added to diesel oil (77.5 ml).

Additive Composition 10

Ethanol	57.2
Ethyl Oleate	42.8
	100.0

Additive Composition 10 (35 ml) was added to diesel oil (65 ml).

The resultant mixtures were allowed to stand to allow the contents to settle. All of the resultant mixtures had a single phase throughout the typical temperature range in which normal fuels are to perform and were found not to be temperature sensitive.

The claims defining the invention are as follows:

1. A fuel blend composition including a hydrocarbon liquid as hereinbefore defined, up to 20% of the total composition of ethanol and/or n-propanol and up to 15% by volume of the total composition of a fatty acid and/or organic ester.

2. A fuel blend composition according to claim 1 wherein the fatty acid and/or organic ester component is between 1.5% - 11% by volume of the total composition.

3. A fuel blend composition according to claim 1 wherein the fatty acid and/or organic ester component is between 2% - 5% by volume of the total composition.

4. A fuel blend composition according to any of claims 1 to 3 wherein the fatty acid is derived from natural oils and fats or vegetable oils or is produced by synthetic means or any mixtures thereof.

5. A fuel blend composition according to claim 4 wherein the natural oils and fats are lard and tallow.

6. A fuel blend composition according to claim 4 wherein the vegetable oils are derived from canola, palm, corn, sunflower oil or soya bean oils.

7. A fuel blend composition according to any of the claims 1 to 3 wherein the organic ester is selected from fatty acids, aromatic esters and/or aliphatic esters and any mixtures thereof.

8. A fuel blend composition according to claim 7, additionally including a dicarboxylic acid ester.

9. A fuel blend composition according to claim 7 wherein the fatty acids are selected from ethyl oleate, methyl oleate, ethyl tallowate, iso-propyl oleate, butyl oleate, methyl oleate or methyl cocoate.

10. A fuel blend composition according to claim 7 wherein the aromatic esters are selected from butyl benzoate and ethyl acetate.

11. A fuel blend composition according to claim 7 wherein the dicarboxylic acid ester is dioctyl maleate.

12. A fuel blend composition according to any of the previous claims further including methanol, iso-propanol, butanol, iso-butanol, tertiary butanol and mixtures thereof.

13. A fuel blend composition according to any of the previous claims wherein the hydrocarbon liquid is at least 40% by volume of the total composition.

14. A fuel blend composition according to any of the previous claims wherein the hydrocarbon liquid is between 75% - 85% by volume of the total composition.

15. A process for producing a single phase fuel blend composition according to any one of claims 1 to 14 including the steps of:

a) adding the ethanol and/or n-propanol alcohol to the hydrocarbon liquid to form an alcohol phase and an oil phase; thereafter

(b) adding the mixture of step (a) to the fatty acid and/or organic ester ; and

(c) mixing the resultant mixture until a single phase is formed.

16. A process for producing a single phase fuel blend according to any one of claims 1 to 14 including the steps of:

(a) adding the ethanol and/or n-propanol to the fatty acid and/or organic ester; thereafter

(b) adding the mixture of step(a) to the hydrocarbon liquid ; and

(c) mixing the resultant mixture until a single phase is formed;

17. A fuel blend composition as hereinbefore described by reference to any of the examples.

18. A fuel additive composition including ethanol and/or n-propanol and a fatty acid and/or organic ester in respective amounts ranging from a ratio of 25:1 to 1:1.

19. A fuel blend composition including the hydrocarbon liquid and up to 35% of the fuel additive composition as in claim 18.

20. A fuel additive composition as hereinbefore described by reference to any of the examples.

International application No.

INTERNATIONAL SEARCH REPORT

PCT/AU 94/00401

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.[5] C10L 1/02, 1/10, 1/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC : C10L 1/02, 1/18

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

AU : IPC as above

Electronic data base consulted during the international search (name of data base, and where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	US,A, 4248182 (MALEC) 3 February 1981 (03.02.81)	(1-4, 9-12)
X	GB,A, 2090612 (INSTITUT FRANCAIS DU PETROLE) 14 July 1982 (14.07.82) See claim 4	(1, 12,13)
A	US,A, 4920691 (FAINMAN) 1 May 1990 (01.05 90)	
A	US,A, 5203878 (WOOMER et al) 20 April 1993 (20.04.93)	

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search	Date of mailing of the international search report
26 September 1994 (26.09.94)	13 Oct 1994 (13.10.94)

Name and mailing address of the ISA/AU

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INTERNATIONAL SEARCH REPORT

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate of the relevant passages	Relevant to Claim No.
A	US,A, 3672854 (ROSENWALD et al) 27 June 1972 (27.06.72)	
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Y,A	GB,A, 2090611 (INSTITUT FRANCAIS DU PETROLE) 14 July 1982 (14.07.82)	(1-13)
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This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report	Patent Flamily Member					
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END OF ANNEX